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EXAMINER

HARLAN, ROBERT D

ART UNIT

PAPER NUMBER

1713

DATE MAILED: 11/15/2006

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BEFORE THE BOARD OF PATENT APPEALS
AND INTERFERENCES

Application Number: 10/782,547
Filing Date: February 19, 2004
Appellant(s): RHODES ET AL.

MAILED
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GROUP 1700

Gwen R. Wood
For Appellant

EXAMINER'S ANSWER

This is in response to the appeal brief filed 08/28/2006
appealing from the Office action mailed 02/13/2006.

Art Unit: 1713

(1) Real Party in Interest

A statement identifying by name the real party in interest is contained in the brief.

(2) Related Appeals and Interferences

The examiner is not aware of any related appeals, interferences, or judicial proceedings which will directly affect or be directly affected by or have a bearing on the Board's decision in the pending appeal.

(3) Status of Claims

The statement of the status of claims contained in the brief is correct.

(4) Status of Amendments After Final

The appellant's statement of the status of amendments after final rejection contained in the brief is correct.

(5) Summary of Claimed Subject Matter

The summary of claimed subject matter contained in the brief is correct.

Art Unit: 1713

(6) Grounds of Rejection to be Reviewed on Appeal

The appellant's statement of the grounds of rejection to be reviewed on appeal is correct.

(7) Claims Appendix

The copy of the appealed claims contained in the Appendix to the brief is correct.

(8) Evidence Relied Upon

6,372,869

ARTHUR ET AL.

4-2002

Art Unit: 1713

(9) Grounds of Rejection

The following ground(s) of rejection are applicable to the appealed claims: Patents are relevant for all they contain. Arthur teaches a process for polymerizing cyclic olefins in the presence of a chain transfer agent. See Arthur, Abstract; col. 7, line 65 through col. 12, line 28. Arthur further teaches the use of Ni metal catalyst formed by contacting mono-dentate ligands with Ni. See Arthur, Example XII. Arthur further teaches phenol derivatives as the mono-dentate ligand. See id.

(10) Response to Argument

The Examiner concurs with Applicant in that Arthur discloses bidentate ligands in a process for the polymerization of a olefin using a polymerization catalyst. However, Arthur also teaches a phenol ligand, which is monodentate. The Applicant has provided a textbook reference disclosing that phenol is an example of a bidentate nucleophile, meaning that the phenol can react at two positions. First, the term "bidentate" is used out of context by the Applicant. While the Examiner agrees that acylation can occur through the "O" or the para "C" (technically acylation can also occur through the ortho "C"), this pertains to substitution reactions, not metal complexes. In metal complexes, only the "O" of the phenol

Art Unit: 1713

ligand complexes with the metal center. There is no simultaneous complexing with another portion of the phenol ligand.

Second, with respect to complex metals or coordination compounds, monodentate ligands are commonly defined as ligands that have only one point of attachment to the metal atom. See Inorganic Chemistry by Shriver et al., Sec. 7.2, W.H. Freeman and Co. (1990); Chemistry, Raymond Chang, Sec. 22.3, WCB McGraw-Hill (1998) (provided as attachments). Based on this definition for "monodentate ligand" placed in the context of metal complexes of ligands to metal centers, not in the context of chemical reactivity of phenols in substitution reactions. One of ordinary skill can clearly determine that a phenol ligand is a monodentate ligand and that Arthur clear teaches the use of phenol, a monodentate ligand, as part of a polymerization catalyst, along with a chain transfer agent in a polymerization process for preparing polycyclic polymers.

Claims 28-30 and 37-40 are rejected for depending on a rejected based claim. Claim 41 is withdrawn from consideration and not under current examination.

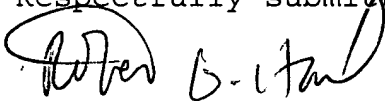
Art Unit: 1713

(11) Related Proceeding(s) Appendix

No decision rendered by a court or the Board is identified by the examiner in the Related Appeals and Interferences section of this examiner's answer.

For the above reasons, it is believed that the rejections should be sustained.

Respectfully submitted,



Robert D. Harlan

Conferees:



David W. Wu

SPE, AU 1713



James Seidleck

SPE, AU 1711

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7.2 Types of ligands and nomenclature

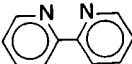
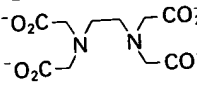
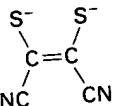
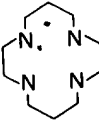
We shall outline here a few key ideas of nomenclature and introduce a number of common ligands. We begin by considering complexes that contain only **monodentate ligands**, ligands that have only one point of attachment to the metal atom, as distinct from **polydentate ligands** which have more than one.

Monodentate ligands

Complexes are named with their ligands (Table 7.2) in alphabetical order. The ligand names are followed by the name of the metal with either its oxidation number in parentheses, as in Co(II) , or with the overall charge on the complex specified in parentheses, as in hexacyanocobaltate(3^-). We add the suffix *-ate* to the name of the metal (sometimes in its Latin form) if the complex is an anion, as in hexacyanoferrate(II) for $[\text{Fe}(\text{CN})_6]^{4-}$.

We should write the formula of a complex inside square brackets whether it is charged or not; however, in casual usage, neutral complexes are often written without brackets, as in $\text{Ni}(\text{CO})_4$. The metal symbol is given first, then the anionic ligands, and finally the neutral ligands. This order is sometimes varied in order to clarify which ligand is involved in a reaction. Polyatomic ligand formulas are sometimes written in an unfamiliar sequence

Table 7.2. Typical ligands and their names

Name	Formula	Abbreviation	Classification*
Acetylacetonato	$\text{CH}_3\text{COCHCOCH}_3^-$	acac	B(O)
Ammine	NH_3		M(N)
2,2-Bipyridine		bipy	B(N)
Carbonato	CO_3^{2-}		M(O), B(O)
Chloro	Cl^-		M(Cl)
Diethylenetriamine	$\text{NH}(\text{C}_2\text{H}_4\text{NH}_2)_2$	dien	T(N)
Ethylenediamine	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	en	B(N)
Ethylenediaminetetraacetato		edta	H(N, O)
Glycinato	$\text{NH}_2\text{CH}_2\text{CO}_2^-$	gly	B(N, O)
Maleonitriledithiolato		mnt	B(S)
Nitrilotriacetato	$\text{N}(\text{CH}_2\text{CO}_2^-)_3$	nta	Q(N, O)
Oxalato	$\text{C}_2\text{O}_4^{2-}$	ox	B(O)
Tetraazacyclotetradecane		cyclam	Q(N)
Triethylenetetramine	$\text{N}(\text{C}_2\text{H}_4\text{NH}_2)_3$	tren	Q(N)

* M: monodentate, B: bidentate, T: tridentate, Q: quadridentate, H: hexadentate.

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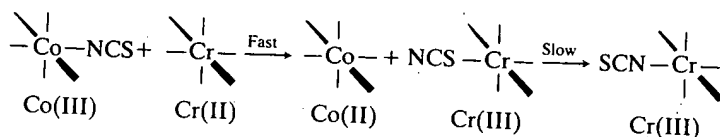
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(as for OH_2 in $[\text{Fe}(\text{OH}_2)_6]^{2+}$) to emphasize the Lewis acid–base character of their bonding to the metal atom.

The number of occurrences of a ligand in a complex is indicated by the prefixes mono-, di-, tri-, and tetra-. Where confusion with the names of ligands is likely (as with ethylenediamine) we use the alternative prefixes bis-, tris-, and tetrakis-, with the ligand name in parentheses. For example, dichloro- or dimethylamino- are clear but bis(methylamine) designates more clearly that there is only one methyl group on each N. Ligands that bridge two metal centers are denoted by μ in front of the name of the relevant ligand. The number of metal atoms in a bridged complex is indicated by the prefixes di-, tri-, etc.

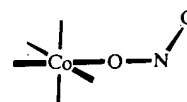
Ambidentate ligands

As we saw in connection with Lewis bases in general (Section 6.3), bases with alternative donor atoms are called **ambidentate**. An example is the thiocyanate ion (NCS^-) which can attach to Cr(III) either by the hard N atom, to give isothiocyanato complexes, or by the softer S atom, to give thiocyanato complexes. Compounds with S—Cr bonds can form in fast reactions in which Cr(II) attacks a Co(III)—NCS complex, as in

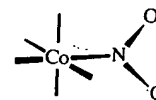


These Cr(III)—SCN thiocyanato complexes are unstable and rearrange to give the Cr(III)—NCS isothiocyanato complex. Two more examples of ambidentate ligands are $-\text{NO}_2^-$ and $-\text{ONO}^-$, and $-\text{SO}_3^{2-}$ and $-\text{OSO}_2^{2-}$.

The existence of ambidentate character gives rise to the possibility of **linkage isomerism**, in which the same ligand is linked through alternative atoms. This type of isomerism accounts for the red and yellow isomers of the formula $[\text{CoNO}_2(\text{NH}_3)_5]^{2+}$. The red compound has a Co—O link (16a) and is called a nitrito complex. The yellow isomer, which forms from the unstable red form on standing, has a Co—N link (16b) and is a nitro complex.



16a



16b

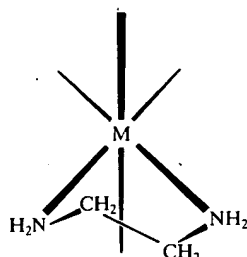
Example 7.3: Naming complexes

Name (a) $[\text{Cr}(\text{edta})]^-$, (b) $\text{trans-}[\text{PtCl}_2(\text{NH}_3)_4]^{2+}$, (c) $[\text{Ni}(\text{CO})_5(\text{py})]$.

Answer. (a) This complex uses hexadentate edta as the sole ligand. The four negative charges of the ligand make an anion of Cr(III) with a single negative charge, namely ethylenediaminetetraacetatochromate(III). (b) The complex is a cation despite its two anionic ligands. Thus, the Pt oxidation number is +4. Following the alphabetical order rules, the name is *trans-tetraamminedichloroplatinum(IV)*. (c) All the ligands are neutral, so the oxidation number of Ni is 0; py is pyridine. The name of the complex is *tricarbonylpyridinenickel(0)*.

Exercise. Give formulas corresponding to the following names: (a) *ethylenediaminetetraacetatoplatinum(II)*; (b) *diamminetetrakis(isothiocyanato)chromate(III)*; (c) *tris(ethylenediamine)rhodium(III)*.

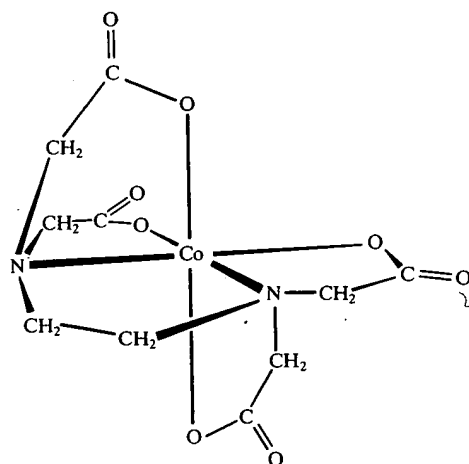
7.2 | d-Metal complexes



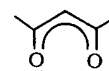
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Chelating ligands

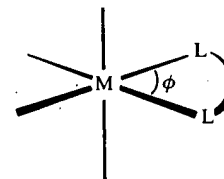
Polydentate ligands are often **chelating** (from the Greek for claw) in that they can form a ring that includes the metal atom. The resulting complex is called a **chelate**. An example is the bidentate ligand ethylenediamine ($\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, en), which forms a five-membered ring (17). A more complex example is the hexadentate ligand ethylenediaminetetraacetic acid (edta) which is used to trap metal ions (18).



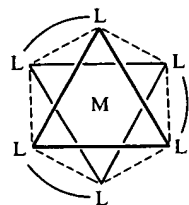
18 $[\text{Co}(\text{edta})]^-$



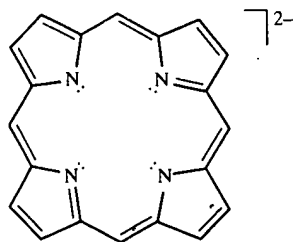
19



20



21



22 Porphyrin

Ring stereochemistry

The $\text{L}-\text{M}-\text{L}$ angle in an octahedral complex is 90° . In a chelate formed from saturated C and N centers, such as (17), the five-membered ring can fold into a conformation that preserves the tetrahedral angles within the ligand and yet still achieve the $\text{L}-\text{M}-\text{L}$ 90° angle. Six-membered rings are reasonably stable and may be favored if electron delocalization (by conjugation of single and double bonds) can then occur. β -Diketones, for example, coordinate as the anions of their enols in six-membered ring structures (19). Amino acids that can form five- or six-membered rings also chelate readily.

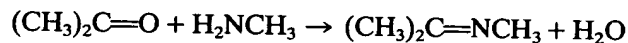
The degree of strain in a chelating ligand can be expressed in terms of the **bite angle** ϕ (20), the $\text{L}-\text{M}-\text{L}$ angle in the chelate ring. The small bite angle for ligands with short donor atom separations is one of the main causes of distortion from octahedral toward trigonal symmetry in six-coordinate complexes (21). However, steric factors do not explain everything. Dithiolene ligands (like those in 7) can produce complexes that are almost trigonal prismatic even though the donor separation is large. In this case it is thought that $\text{S}_\pi-\text{S}$ bonding straps the donor atoms together and hence favors a twisting of the octahedron.

A special case of the chelation occurs with a **macrocyclic ligand**, a polydentate ligand in which several donor atoms form a large ring even before the complex is formed. An example is the porphyrin ring (22), which is found (in modified forms) complexed with Fe at the oxygen-binding site

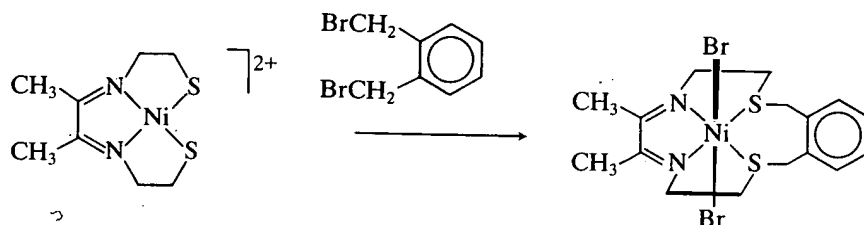
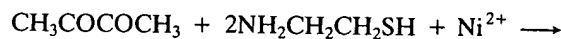
of hemoglobin and with Mg in chlorophyll. A number of electron-transfer enzymes are Fe porphyrins. A saturated analog of the porphyrin ligand is tetraazacyclotetradecane (called familiarly 'cyclam', Table 7.2).

Template synthesis

A metal ion such as Ni(II) can be used to assemble a group of ligands which then undergo a condensation reaction to form a macrocyclic ligand. (In a condensation reaction a bond is formed between two molecules, and a small molecule—often H₂O—is eliminated.) This trick, which is called **template synthesis**, can be applied to produce a surprising variety of macrocyclic ligands. The most generally useful condensation reaction is the Schiff's base condensation of an amine and a ketone, of which an example is



(A Schiff's base, an *anil*, is the product $\text{R}_2\text{C}=\text{N}-\text{R}'$.) A good example of a template synthesis is the reaction that follows coordination of one butadione molecule and two 1,2-aminoethylthiol molecules to Ni(II). This complex then condenses with 1,2-di(bromomethyl)benzene to form a macrocycle:



7.3 Chiral complexes

A **chiral** complex is a complex that is not superimposable on its own mirror image. The formal criterion of chirality (Section 2.4) is the absence of an axis of improper rotation (S_n , an n -fold axis in combination with a horizontal mirror plane). The presence of such a symmetry element is implied by the presence of either a mirror plane (which is equivalent to an S_1 axis) or a center of inversion (which is equivalent to an S_2 axis), and if either of these elements is present the complex is achiral. As remarked in Section 2.4, we must also be alert for higher-order axes of improper rotation (particularly S_4), since the presence of any S_n axis implies achirality.

Optical isomerism

The existence of a pair of distinct chiral isomeric complexes that are each other's mirror image (like a right and left hand), and which have lifetimes that are long enough for them to be separable, is called **optical isomerism**. The two mirror-image isomers jointly make up an **enantiomeric pair**. Optical isomers are so called because they are optically active, in the sense that one enantiomer rotates the plane of polarized light in one direction and the other rotates it through an equal angle in the opposite direction.

With Co(III), for example, ethylenediamine forms a violet and green pair

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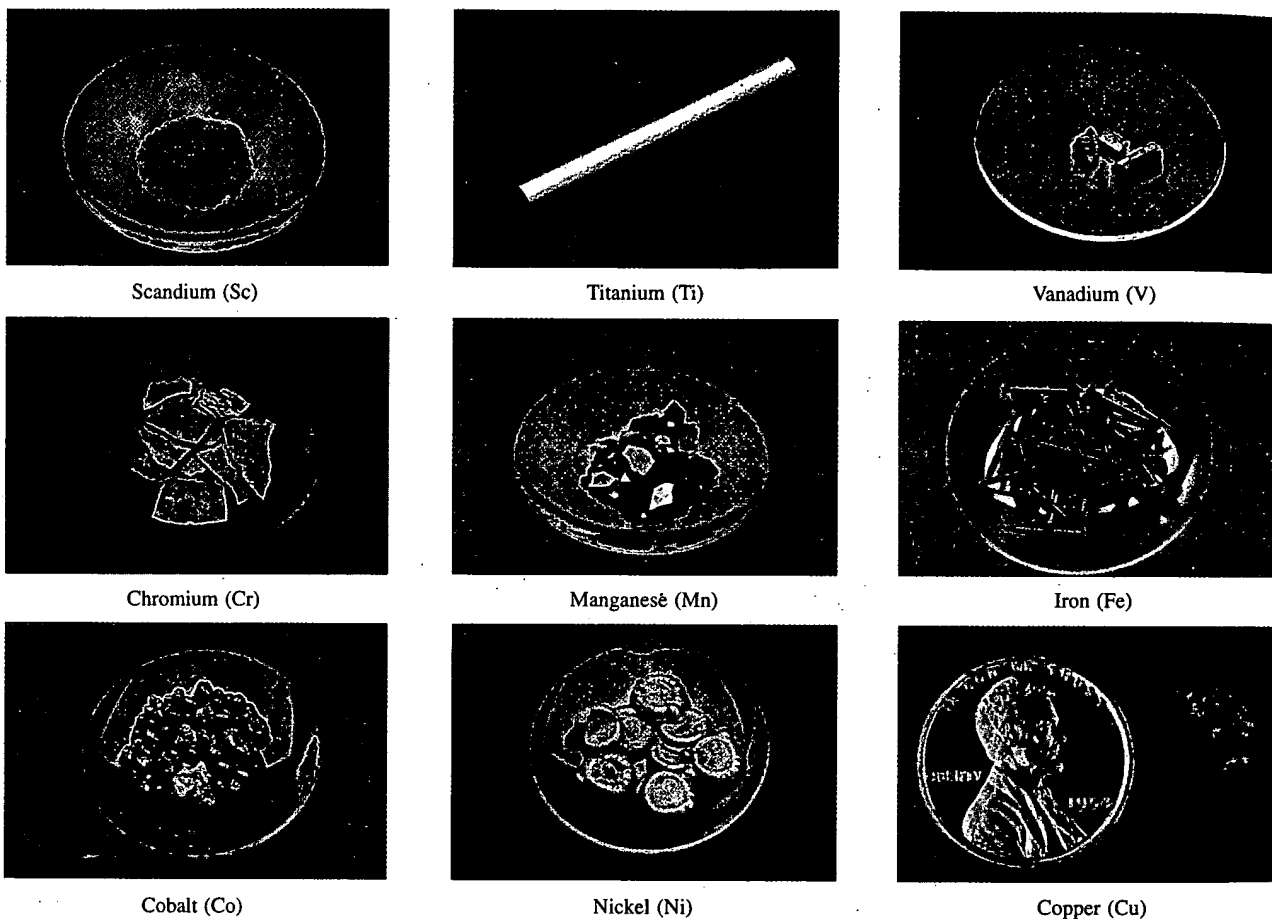


FIGURE 22.4 The first-row transition metals.

Impure copper can be purified by electrolysis (see Section 20.2). After silver, which is too expensive for large-scale use, copper has the highest electrical conductivity. It is also a good thermal conductor. Copper is used in alloys, electrical cables, plumbing (pipes), and coins.

Copper reacts only with hot concentrated sulfuric acid and nitric acid (see Figure 21.9). Its two important oxidation states are +1 and +2. The +1 state is less stable and disproportionates in solution:



All compounds of Cu(I) are diamagnetic and colorless except for Cu_2O , which is red. The Cu(II) compounds are all paramagnetic and colored. The hydrated Cu^{2+} ion is blue. Some important Cu(II) compounds are CuO (black), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (blue), and CuS (black).

22.3 COORDINATION COMPOUNDS

Recall that a complex ion contains a central metal ion bonded to one or more ions or molecules (see Section 16.10).

Transition metals have a distinct tendency to form complex ions, which in turn can combine with other ions or complex ions to form coordination compounds. A *coordination compound* is a neutral species containing one or more complex ions. Our understanding of the nature of coordination compounds stems from the classic work of

Alfred Werner,[†] who prepared and characterized many coordination compounds. In 1893, at the age of 26, Werner proposed what is now commonly referred to as *Werner's coordination theory*.

Nineteenth-century chemists were puzzled by a certain class of reactions that seemed to violate valence theory. For example, the valences of the elements in cobalt(III) chloride and in ammonia seem to be completely satisfied, and yet these two substances react to form a stable compound having the formula $\text{CoCl}_3 \cdot 6\text{NH}_3$. To explain this behavior, Werner postulated that most elements exhibit two types of valence: *primary valence* and *secondary valence*. In modern terminology, primary valence corresponds to the oxidation number and secondary valence to the coordination number of the element. In $\text{CoCl}_3 \cdot 6\text{NH}_3$, according to Werner, cobalt has a primary valence of 3 and a secondary valence of 6.

Today we use the formula $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ to indicate that the ammonia molecules and the cobalt atom form a complex ion; the chloride ions are not part of the complex but are held to it by ionic forces. Most, but not all, of the metals in coordination compounds are transition metals.

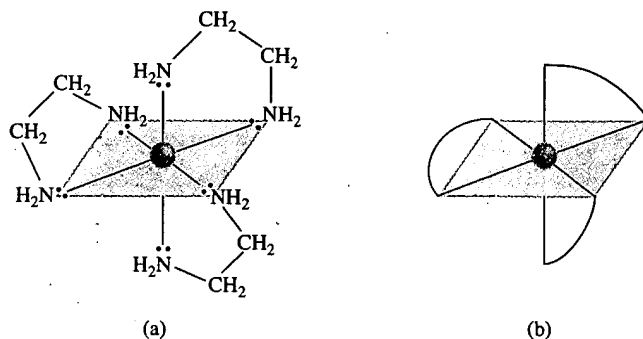
The molecules or ions that surround the metal in a complex ion are called *ligands* (Table 22.3). The interactions between a metal atom and the ligands can be thought of

[†]Alfred Werner (1866–1919). Swiss chemist. Werner started as an organic chemist but became interested in coordination chemistry. For his theory of coordination compounds, Werner was awarded the Nobel Prize in Chemistry in 1913.

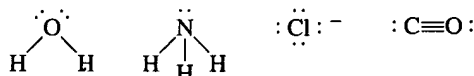
TABLE 22.3 Some Common Ligands

NAME	STRUCTURE
<i>Monodentate ligands</i>	
Ammonia	$\begin{array}{c} \text{H}-\ddot{\text{N}}-\text{H} \\ \\ \text{H} \end{array}$
Carbon monoxide	$:\text{C}\equiv\text{O}:$
Chloride ion	$:\ddot{\text{Cl}}:^-$
Cyanide ion	$[\text{:C}\equiv\text{N:}]^-$
Thiocyanate ion	$[\text{:S}-\text{C}\equiv\text{N:}]^-$
<i>Bidentate ligands</i>	
Ethylenediamine	$\text{H}_2\ddot{\text{N}}-\text{CH}_2-\text{CH}_2-\ddot{\text{N}}\text{H}_2$
Oxalate ion	$\left[\begin{array}{cc} \text{O} & \text{O} \\ \parallel & \parallel \\ \text{C} & - & \text{C} \\ \parallel & \parallel \\ \text{O} & \text{O} \end{array} \right]^{2-}$
<i>Polydentate ligand</i>	
Ethylenediaminetetraacetate ion (EDTA)	$\left[\begin{array}{ccc} \text{O} & & \text{O} \\ \parallel & & \parallel \\ \text{O}-\text{C} & \text{CH}_2 & \text{C}-\text{O} \\ & & \\ \text{O} & \text{N}-\text{CH}_2-\text{CH}_2-\text{N} & \text{O} \\ & & \\ \text{O} & \text{CH}_2 & \text{C} \\ \parallel & & \parallel \\ \text{O} & & \text{O} \end{array} \right]^{4-}$

FIGURE 22.7 (a) Structure of metal-ethylenediamine complex. Each ethylenediamine molecule provides two N donor atoms and is therefore a bidentate ligand. (b) Simplified structure of the same complex.



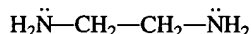
as Lewis acid-base reactions. As we saw in Section 15.12, a Lewis base is a substance capable of donating one or more electron pairs. Every ligand has at least one unshared pair of valence electrons, as these examples show:



Therefore, ligands play the role of Lewis bases. On the other hand, a transition metal atom (in either its neutral or positively charged state) acts as a Lewis acid, accepting (and sharing) pairs of electrons from the Lewis bases. Thus the metal-ligand bonds are usually coordinate covalent bonds (see Section 9.9).

The atom in a ligand that is bound directly to the metal atom is known as the **donor atom**. For example, nitrogen is the donor atom in the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex ion. The **coordination number** in coordination compounds is defined as the number of donor atoms surrounding the central metal atom in a complex ion. For example, the coordination number of Ag^+ in $[\text{Ag}(\text{NH}_3)_2]^+$ is 2, that of Cu^{2+} in $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is 4, and that of Fe^{3+} in $[\text{Fe}(\text{CN})_6]^{3-}$ is 6. The most common coordination numbers are 4 and 6, but coordination numbers such as 2 and 5 are also known.

Depending on the number of donor atoms present, ligands are classified as *monodentate*, *bidentate*, or *polydentate* (see Table 22.3). H_2O and NH_3 are monodentate ligands with only one donor atom each. One bidentate ligand is ethylenediamine (sometimes abbreviated “en”):



The two nitrogen atoms can coordinate with a metal atom as shown in Figure 22.7.

Bidentate and polydentate ligands are also called **chelating agents** because of their ability to hold the metal atom like a claw (from the Greek *chele*, meaning “claw”). One example is ethylenediaminetetraacetate ion (EDTA), a polydentate ligand used to treat metal poisoning (Figure 22.8). Six donor atoms enable EDTA to form a very stable complex ion with lead. In this form it is removed from the blood and tissues and excreted from the body. EDTA is also used to clean up spills of radioactive metals.

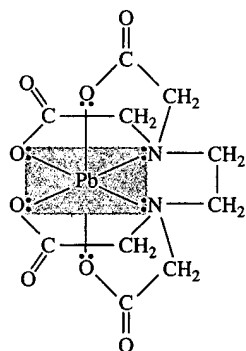


FIGURE 22.8 EDTA complex of lead. The complex bears a net charge of -2 , since each O donor atom has one negative charge and the lead ion carries two positive charges. Note the octahedral geometry around the Pb^{2+} ion.

OXIDATION NUMBERS OF METALS IN COORDINATION COMPOUNDS

Another important property of coordination compounds is the oxidation number of the central metal atom. The net charge of a complex ion is the sum of the charges on the central metal atom and its surrounding ligands. In the $[\text{PtCl}_6]^{2-}$ ion, for example, each

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chloride ion has an oxidation number of -1 , so the oxidation number of Pt must be $+4$. If the ligands do not bear net charges, the oxidation number of the metal is equal to the charge of the complex ion. Thus, in $[\text{Cu}(\text{NH}_3)_4]^{2+}$ each NH_3 is neutral, so the oxidation number of Cu is $+2$.

Example 22.1 deals with oxidation numbers of metals in coordination compounds.

EXAMPLE 22.1

Specify the oxidation number of the central metal atom in each of the following compounds: (a) $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_2$, (b) $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_3$, (c) $[\text{Fe}(\text{CO})_5]$, (d) $\text{K}_4[\text{Fe}(\text{CN})_6]$.

Answer (a) Both NH_3 and H_2O are neutral species. Since each chloride ion carries a -1 charge, and there are two Cl^- ions, the oxidation number of Ru must be $+2$. (b) Each nitrate ion has a charge of -1 ; therefore, the cation must be $[\text{Cr}(\text{NH}_3)_6]^{3+}$. NH_3 is neutral, so the oxidation number of Cr is $+3$. (c) Since the CO species are neutral, the oxidation number of Fe is zero. (d) Each potassium ion has a charge of $+1$; therefore, the anion is $[\text{Fe}(\text{CN})_6]^{4-}$. Next, we know that each cyanide group bears a charge of -1 , so Fe must have an oxidation number of $+2$.

PRACTICE EXERCISE

Write the oxidation numbers of the metals in the compound $\text{K}[\text{Au}(\text{OH})_4]$.

Similar problems: 22.13, 22.14.

NAMING COORDINATION COMPOUNDS

Now that we have discussed the various types of ligands and the oxidation numbers of metals, our next step is to learn what to call these coordination compounds. The rules for naming coordination compounds are as follows:

- The cation is named before the anion, as in other ionic compounds. The rule holds regardless of whether the complex ion bears a net positive or a negative charge. For example, in $\text{K}_3[\text{Fe}(\text{CN})_6]$ and $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ compound, we name the K^+ and $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ cations first, respectively.
- Within a complex ion the ligands are named first, in alphabetical order, and the metal ion is named last.
- The names of anionic ligands end with the letter *o*, whereas a neutral ligand is usually called by the name of the molecule. The exceptions are H_2O (aquo), CO (carbonyl), and NH_3 (ammine). Table 22.4 lists some common ligands.
- When several ligands of a particular kind are present, we use the Greek prefixes *di-*, *tri-*, *tetra-*, *penta-*, and *hexa-* to name them. Thus the ligands in the cation $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$ are "tetraamminedichloro." (Note that prefixes are ignored when alphabetizing ligands.) If the ligand itself contains a Greek prefix, we use the prefixes *bis* (2), *tris* (3), and *tetrakis* (4) to indicate the number of ligands present. For example, the ligand ethylenediamine already contains *di*; therefore, if two such ligands are present the name is *bis(ethylenediamine)*.
- The oxidation number of the metal is written in Roman numerals following the name of the metal. For example, the Roman numeral III is used to indicate the $+3$ oxidation state of chromium in $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$, which is called tetraamminedichlorochromium(III) ion.